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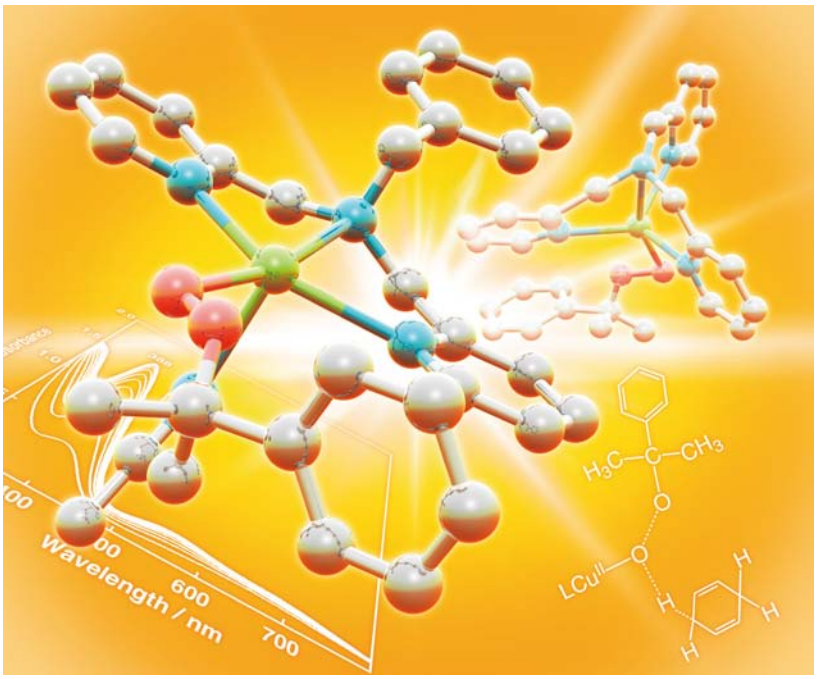

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PAPER

Redox reactivity of photogenerated osmium(II) complexes†

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Powerful reductants $[Os^{II}(NH_3)_5L]^{2+}$ (L = OH_2, CH_3CN) can be generated upon ultraviolet excitation of relatively inert $[Os^{II}(NH_3)_5(N_2)]^{2+}$ in aqueous and acetonitrile solutions. Reactions of photogenerated Os(II) complexes with methyl viologen to form methyl viologen radical cation and $[Os^{III}(NH_3)_5L]^{3+}$ were monitored by transient absorption spectroscopy. Rate constants range from 4.9×10^4 M^{-1} s^{-1} in acetonitrile solution to 3.2×10^7 (pH 3) and 2.5×10^8 M^{-1} s^{-1} (pH 12) in aqueous media. Photogeneration of five-coordinate Os(II) complexes opens the way for mechanistic investigations of activation/reduction of CO_2 and other relatively inert molecules.

Introduction

Over 30 years ago, Ford and coworkers reported that a powerful reductant, $[Os^{II}(NH_3)_5(OH_2)]^{2+}$, can be generated by ultraviolet excitation (229–365 nm)[1,2] of aqueous solutions of a relatively inert Os(II)-dinitrogen complex, $[Os^{II}(NH_3)_5N_2]^{2+}$.[3–5] Of special interest is that this photogenerated Os(II) complex reacted with solvent, yielding Os(III) products.[1,2] A very large increase in the acidity of coordinated water accompanied oxidation of the Os(II) aquo complex: estimates of the pK_a of $[Os^{II}(NH_3)_5(OH_2)]^{2+}$ range from 10 and 12, whereas the corresponding Os(III) species is acidic (4.85).[6,7] Thus, only at low pH will the aquo ligand be protonated in both oxidation states (a reduction potential of –0.73 V *vs.* NHE for $[Os(NH_3)_5(OH_2)]^{3+}$ has been reported).[6,8] Above pH 4.85, the formal potential varies as predicted for a 1 e^-/1 H^+ process: Os(II) is protonated, but Os(III) is not.[7] Although electrochemical data for $[Os(NH_3)_5(OH)]^{2+/+}$ under strongly basic conditions have not been reported, extrapolated pH 10 and 12 values provide estimated $[Os(NH_3)_5(OH)]^{2+/+}$ potentials of *ca.* –1.03 and –1.15 V, respectively.

Rapid photogeneration of $[Os^{II}(NH_3)_5L]^{2+}$ (L = OH_2, CH_3CN) opens the way for investigations of the chemistry of these powerful reductants, including reaction of the aquo complex to produce $[Os^{III}(NH_3)_5(OH)]^{2+}$.[9–11] Here we report the kinetics of reactions of these Os(II) complexes with methyl viologen [MV^{2+}, $E^0(MV^{2+/\bullet+})$ = –0.45 V *vs.* NHE in H_2O][12] in acetonitrile and aqueous solutions. We also consider mechanisms that might account for surprising reactivity variations that are observed in different media.

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Results and discussion

Irradiation of a sample containing $[Os^{II}(NH_3)_5N_2]Cl_2$ and $[MV]Cl_2$ in neutral buffered aqueous solution (100 mM NaP*i*) led to irreversible formation of $MV^{\bullet+}$ (λ_{ex} = 355 nm). The growth of new absorption features at 393 and 605 nm, characteristic of the viologen radical, is seen in steady-state absorbance spectra measured at intervals during photolysis (Fig. 1).[13] Similar behavior was observed at other pHs, as well as in dry acetonitrile (100 mM [^{n}Bu$_4$N][PF_6], ESI†).

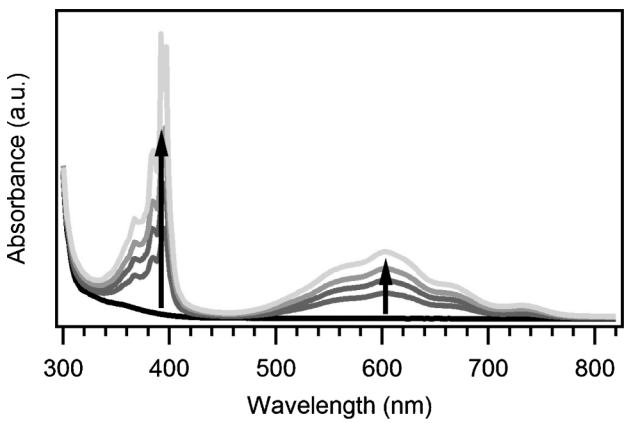

Fig. 1 Steady-state absorbance spectra obtained at intervals upon irradiation (λ = 355 nm) of $[Os(NH_3)_5N_2]Cl_2$ and $[MV]Cl_2$ in aqueous solution indicate the formation of reduced methyl viologen ($MV^{\bullet+}$). Sample conditions: 1.6 mM $[Os(NH_3)_5N_2]Cl_2$, 1.2 mM $[MV]Cl_2$, 100 mM NaP*i*, pH 7.

By monitoring transient absorption (λ_{obs} = 610 nm), we obtained kinetics of electron transfer from photogenerated $[Os^{II}(NH_3)_5L]^{2+}$ (L = OH_2, CH_3CN) complexes to MV^{2+} (Fig. 2). The formation of $MV^{\bullet+}$ is best fit to single exponential kinetics, and the first-order rate constant is linearly dependent on the concentration of

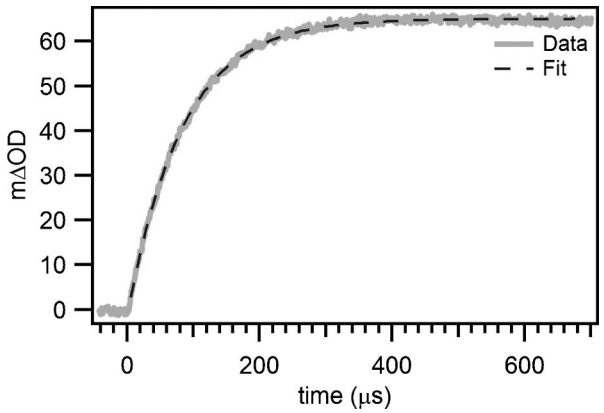

Fig. 2 Transient kinetics trace monitoring the appearance of $MV^{\bullet+}$ upon photochemical generation of $[Os(NH_3)_5(OH_2)]^{2+}$ (λ_{ex} = 355 nm, λ_{obs} = 610 nm) fit to single exponential kinetics. Conditions: 1.7 mM $[Os(NH_3)_5N_2]Cl_2$, 0.36 mM $[MV]Cl_2$, 100 mM NaP*i*, pH 3.

MV^{2+} under these pseudo-first-order conditions (methyl viologen in excess of photogenerated $[Os^{II}(NH_3)_5L]^{2+}$), allowing second-order rate constants for electron transfer to be estimated.

The apparent second-order rate constant for reduction of $[MV][PF_6]_2$ by $[Os^{II}(NH_3)_5(CH_3CN)]^{2+}$ in dry acetonitrile solution is 4.9×10^4 M^{-1} s^{-1} (Fig. 3). The plot of observed rate constant *versus* $[MV^{2+}]$ is linear, but the intercept is larger than expected for a simple bimolecular reaction. The reduction potentials of osmium(III) pentaammine nitrile complexes are substantially more positive than those of corresponding aquo species. Taube and coworkers reported $E_{\frac{1}{2}}$ values of –0.29 V *vs.* NHE for $[Os^{III}(NH_3)_5(CH_3CN)]^{3+}$ in glyme,[14] and –0.25 V *vs.* NHE in aqueous solution.[15] The MV^{2+} reduction potential in aqueous solution (–0.45 V *vs.* NHE) indicates that reduction by $[Os^{II}(NH_3)_5(CH_3CN)]^{2+}$ in this medium is endergonic. It is likely that the reaction in acetonitrile is endergonic as well, but uncertainties in reduction potentials for these ions in this aprotic solvent preclude a firm conclusion on this point.[16] The finite intercept in the plot of observed rate constant *versus* $[MV^{2+}]$ may be a consequence of a reaction that is an approach to equilibrium rather than a straightforward bimolecular process (see ESI†).

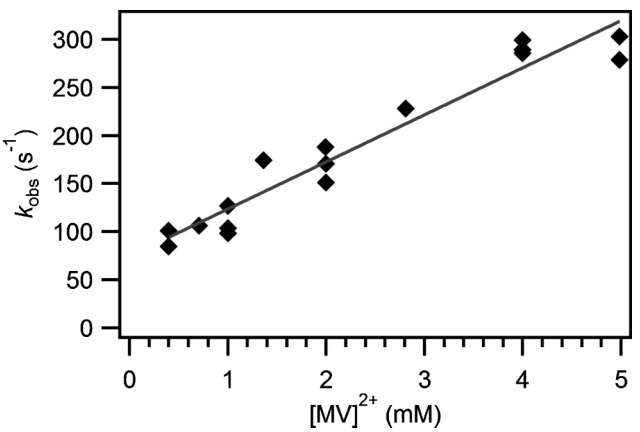

Fig. 3 Linear relationship between observed first-order rate constants and oxidative quencher concentrations for reaction of MV^{2+} with $[Os(NH_3)_5(CH_3CN)]^{2+}$ in acetonitrile solution: $k_{obs} = k_0 + k_{ET}[MV^{2+}]$, k_0 = 75 s^{-1}, $k_{ET} = 4.9 \times 10^4$ M^{-1} s^{-1}. Sample conditions: 3.5 mM $[Os(NH_3)_5N_2][PF_6]_2$, varying concentrations of $[MV][PF_6]_2$, 100 mM $[^nBu_4N][PF_6]$.

Reduction of methyl viologen by Os(II) is much faster in aqueous solutions. Under conditions (pH 3) when the aquo species is protonated in both Os(II) and Os(III) oxidation states, we estimate a driving force of *ca.* 280 meV for oxidation of $[Os^{II}(NH_3)_5(OH_2)]^{2+}$ by MV^{2+}. A second-order rate constant of 3.2×10^7 M^{-1} s^{-1} was obtained for this redox reaction (Fig. 4).

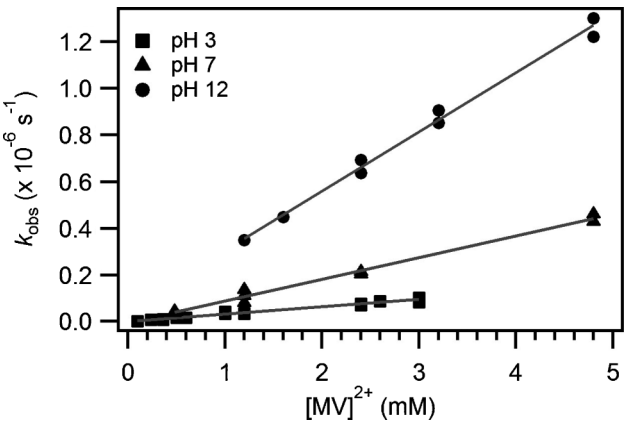

Fig. 4 Linear relationships between observed first-order rate constants and oxidative quencher concentrations for formation of $MV^{\bullet+}$ from reaction of $[Os(NH_3)_5(OH_2)]^{2+}$ with MV^{2+} at pH 3, 7, and 12: $k_{obs} = k_0 + k_{ET}[MV^{2+}]$. pH 3: $k_0 = 1.8 \times 10^3$ s^{-1}, $k_{ET} = 3.2 \times 10^7$ M^{-1} s^{-1}; pH 7: $k_0 = -3.8 \times 10^3$ s^{-1}, $k_{ET} = 9.3 \times 10^7$ M^{-1} s^{-1}; pH 12: $k_0 = 5.5 \times 10^4$ s^{-1}, $k_{ET} = 2.5 \times 10^8$ M^{-1} s^{-1}. Sample conditions: 1.7–3.5 mM $[Os(NH_3)_5N_2]Cl_2$, varying concentrations of $[MV]Cl_2$, 100 mM NaP*i*.

Photolysis of $[Os^{II}(NH_3)_5N_2]^{2+}$ in aqueous media at pH 12 produces an osmium(II) hydroxo species, $[Os^{II}(NH_3)_5(OH)]^+$, which is a more powerful reductant than $[Os^{II}(NH_3)_5(OH_2)]^{2+}$ (the driving force for electron transfer from $[Os^{II}(NH_3)_5(OH)]^+$ to MV^{2+} is *ca.* 580–700 meV). The second-order rate constant (2.5×10^8 M^{-1} s^{-1}) is an order of magnitude larger than that obtained for reaction of the aquo species at pH 3 (Fig. 4).

At neutral pH, a rate constant of 9.3×10^7 M^{-1} s^{-1} was obtained (Fig. 4). While proton loss is expected to accompany electron transfer from $[Os^{II}(NH_3)_5(OH_2)]^{2+}$ to MV^{2+}, which would give $[Os^{III}(NH_3)_5(OH)]^{2+}$ at pH 7, we did not expect to find a pH-dependent rate constant.[17] We propose that the buffer, HPO_4^{2-}, acts as proton acceptor in these reactions.[18–20] We note that Finklea and Savéant have investigated other proton-coupled electron transfer processes in related $Os^{II}(OH_2)/Os^{III}(OH)$ complexes.[21–24]

The classical theory of electron transfer reactions (eqn (1))

$$k = Ze^{-\frac{w_r}{RT}} e^{-\frac{(\Delta G^\circ + w_r - w_p + \lambda)^2}{4\lambda RT}} \quad (1)$$

predicts that bimolecular rate constants will depend on: the collision frequency of molecules in solution ($Z \sim 10^{11}$ $M^{-1}s^{-1}$); the work required to bring reactants (w_r) and products (w_p) to the mean donor–acceptor separation distance; the standard free energy of reaction (ΔG^0); and the nuclear reorganization energy (λ).[25] Neglecting work terms associated with precursor–complex formation, and assuming λ is constant for reactions of $[Os^{II}(NH_3)_5(OH)]^+$ and $[Os^{II}(NH_3)_5(OH_2)]^{2+}$ with MV^{2+}, the ratio of rate constants obtained at pH 12 and 3 leads to an estimated

reorganization energy of 0.65 eV. The lower work required to assemble the precursor complex at pH 12 will produce a further reduction in estimated reorganization energy.

The increase in electron transfer rate constant upon raising the pH from 3 to 12 is relatively modest, requiring a λ value that is substantially smaller than expected for reactions of Os ammine complexes with MV^{2+}. Brown and Sutin reported a self-exchange reorganization energy of 1.3 eV for $Ru(NH_3)_6^{3+/2+}$; comparable values are expected for Os ammine complexes.[26] The ≤0.65-eV λ for a cross reaction between $[Os^{II}(NH_3)_5(OH_2)]^{2+}$ and MV^{2+} implies an unreasonably small self-exchange reorganization energy for the $MV^{2+/\bullet+}$ couple (~0 eV, $\lambda_{12} = \frac{1}{2}\lambda_{11} + \frac{1}{2}\lambda_{22}$). Moreover, the driving force at pH 12 (580–700 meV) should lead to a negligible barrier to electron transfer, yet the experimentally determined rate constant (2.5×10^8 M^{-1} s^{-1}) is smaller than that expected for diffusion limited processes ($k \approx 10^{10}$ M^{-1} s^{-1}). These inconsistencies with classical theory suggest that electron transfers from $[Os^{II}(NH_3)_5(OH_2)]^{2+}$ and/or $[Os^{II}(NH_3)_5(OH)]^{+}$ to MV^{2+} may not be simple outer-sphere bimolecular reactions. Finn and coworkers have suggested that $[Os^{II}(NH_3)_5(OH_2)]^{2+}$ rapidly converts to a species that functions as an Os(II) synthon prior to reactivity.[27] The authors speculated that this species may be an osmium hydride, $[Os^{IV}(NH_3)_5(OH)(H)]^{2+}$. If such a hydride were an intermediate in the reactions at pH 3, deprotonation of $[Os^{IV}(NH_3)_5(OH)(H)]^{2+}$ would be required prior to electron transfer to MV^{2+}. This additional step preceding electron transfer should have reduced the observed rate constant at pH 3, leading to a greater increase in specific rate upon raising the pH. It is unlikely, therefore, that hydride formation can account for the relatively flat driving force (*i.e.*, pH) dependence of electron transfer rates.

Irrespective of the uncertainties associated with electron transfer mechanistic details, it is clear that ultraviolet irradiation of Os(II) dinitrogen complexes efficiently labilizes the N_2 ligand to produce powerful Os(II) reductants. In coordinating solvents such as water and acetonitrile, ligand exchange occurs to form $[Os^{II}(NH_3)_5L]^{2+}$ (L = OH_2, CH_3CN). In the presence of methyl viologen, electron transfer from Os(II) to MV^{2+} gives $MV^{\bullet+}$ and $[Os^{III}(NH_3)_5L]^{3+}$, likely *via* an unidentified Os(II) intermediate. In weakly coordinating solvents (*e.g.*, CH_3OH), the Os ammine fragment produced by photolysis might be induced to react with refractory substrates such as CO_2.

Experimental

Reagents

Tetrabutylammonium hexafluorophosphate was recrystallized from ethanol. $[Os(NH_3)_5N_2]Cl_2$ was obtained from Aldrich and recrystallized from HCl per the method of Allen and Stevens and washed with diethyl ether.[4] The hexafluorophosphate salts of $[Os(NH_3)_5N_2]^{2+}$ and MV^{2+} were prepared from the corresponding chloride salts *via* metathesis in water (0 °C), then washed with diethyl ether and dried under vacuum. 100 mM NaP*i* buffers were prepared from H_3PO_4, NaH_2PO_4, Na_2HPO_4 and adjusted to pH 3, 7, or 12 with NaOH.

Aqueous samples were placed into the cell of a high-vacuum 1-cm pathlength fused quartz cuvette (Starna Cells) isolated from atmosphere by a high-vacuum Teflon valve (Kontes). Samples were degassed by exposure to vacuum with stirring and placed under an argon atmosphere 10 times to remove oxygen from the solution.

Acetonitrile samples were prepared in a N_2 filled glove box with acetonitrile that had been deoxygenated and dried by thorough sparging with N_2 followed by passage through an activated alumina column. Samples were placed into the cell of a high-vacuum 1-cm pathlength fused quartz cuvette (Starna Cells) and isolated from atmosphere and the bulb by a high-vacuum Teflon valve (Kontes).

Physical methods

UV-visible absorption measurements were carried out using a Hewlett Packard 8452 UV-Vis spectrophotometer in 1 cm pathlength quartz cuvettes.

Time-resolved spectroscopic measurements were carried out at the Beckman Institute Laser Resource Center. 355-nm laser excitation was provided by 8-ns pulses from the third harmonic of a 10 Hz Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series). Pulse powers ranged from 1–10 mJ/pulse. Probe light for transient absorption measurements was provided by a 75-W arc lamp (PTI Model A 1010) that operated in continuous wave or pulsed modes. Probe light was filtered (550-nm long-pass) prior to passing through the sample collinearly with the laser excitation beam. Scattered excitation light was rejected by suitable long pass filters, and probe wavelengths were selected for detection by a double monochromator (Instruments SA DH-10) with 1-mm slits. Transmitted probe light was detected with a photomultiplier tube (PMT, Hamamatsu R928). The PMT current was amplified and recorded with a GageScope transient digitizer. The data were converted to units of ΔOD ($\Delta OD = -\log_{10}(I/I_0)$; I is the time-resolved probe-light intensity with laser excitation; I_0 is the intensity without excitation). Transient absorption measurements on microsecond and shorter timescales were performed with 10-Hz excitation on continuously stirred samples. Measurements on longer timescales involved a 4-step event sequence: one shutter-released laser pulse; data recording; 1 s of sample stirring; 2 s dwell period for solution settling prior to release of the next laser pulse. Data were averaged over approximately 15–100 laser shots. All instruments and electronics in were controlled by software written in LabVIEW (National Instruments). Data were log-time compressed prior to fitting. Data manipulation was performed with MATLAB R2008a (Mathworks, Inc.) and graphed with Igor Pro 5.01 (Wavemetrics).

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